Automated Trace Metals Analyzer

Space and Naval Warfare Systems Center, San Diego
Environmental Sciences Division, Code 236

March 18, 2002

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San Diego, California

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1. Introduction

1.1   Background Information

In industrial process control and environmental compliance monitoring, graphite furnace atomic absorption (GFAA) spectroscopy and inductively coupled plasma (ICP) mass spectroscopy have been traditionally used to measure trace metals. These instruments are large, expensive, and require a high level of infrastructure support. Because of this, trace metal measurement usually involves sampling, preservation, and transport to a centralized laboratory for later analysis. Current field tests for metals are difficult to use under industrial conditions, usually lack simultaneous multianalyte capability, and require significant operator intervention.

The Automated Trace Metals Analyzer (ATMA) enables near real-time (one sample/5 min), unattended on-site measurement of trace metals, such as lead, copper, mercury, arsenic, and cadmium in aqueous media. It will reduce analytical costs over conventional monitoring, and enable near real-time industrial process monitoring.

This automated instrument is designed for unattended collection and analysis of trace levels of heavy metals in water. The ATMA measures metal contamination using Potentiometric Stripping Analysis (PSA). PSA is capable of measuring multiple metals simultaneously at environmentally relevant concentrations. This instrument will allow users to make on the spot or continuos long-term measurements of metal contamination in an unattended automated mode. The ATMA can be set up to take measurements at timed intervals or in response to an eternal trigger.

The ATMA's windows based interface enable non-technical personnel to setup the instrument and collect data with minimal training. The instrument continually monitors performance and will automatically notify the operator and log any problems that it cannot correct. While in operation the instrument is sealed from the external environment excluding the possibility of sample contamination. The instrument is also allows non-technical personnel to operate it in an on-site, discrete analyses mode. This capability will permit expanded monitoring in support of efforts where diverse sources must be frequently monitored over extended periods at a low cost.

1.2   Official DoD Requirement Statement
The demonstration of the ATMA technology falls under the ESTCP Focus area 4. Compliance, sub area 1. Emission/Waste Characterization and Monitoring.

1.2.2   How Requirement was Addressed. The ATMA was used in two types of wastewater treatment systems. The first was a traditional manual batch tank treatment process where flocculent is manually added to a tank of wastewater and the precipitates containing the metals are allowed to settle out. The second system was a continuous flow through system utilizing advanced Molecular Recognition (MRT) technology.

1.3   Objectives of the Demonstration

The objective of this demonstration is to provide performance, cost and field data for user acceptance. To meet these objectives this project is divided into two major thrusts, field demonstration and laboratory validation. Validation of the instrument involves collecting data, which will define the accuracy, precision and sensitivity of the instrument. Field demonstration will gather "actual" use data such as operator and expendable cost using the ATMA verses the traditional laboratory sample-and-ship method.

In this demonstration the ATMA was used to measure the trace metals levels at the North Island Naval Air Station Industrial Wastewater Treatment Plant (IWTP) batch process and to measure online in real-time the metal concentrations of the Molecular Recognition Technology (MRT) demonstration system at the Puget Sound Naval Ship Yard (PSNSY) IWTP. These results were compared to the standard graphite furnace atomic absorption spectrometry (GF-AA) and inductively coupled plasma mass spectrometry (ICP-MS).

1.4   Regulatory Issues

On October 6, 1997 EPA published a notice [Federal Register: October 6, 1997 (Volume 62, Number 193, pages 52098-52100)] that it plans to adopt a fundamentally different approach to environmental monitoring, known as a "performance based measurement system ". Rather than requiring that a prescribed analytical method be used for a particular measurement, under the new approach any method could be used provided that it is demonstrated to meet required performance standards. EPA believes that this approach will be more flexible and more cost-effective for the regulated community and that it will encourage innovation in analytical technology and improve data quality. This approach will allow the use of technology such as the ATMA in monitoring without costly and time-consuming method approval previously required under the old system.

In these demonstrations the ATMA is used as a process monitor to ensure that regulatory requirements are met. The ATMA did not substitute for the permitted measurements.

1.5   Previous Testing of the Technology

PSA technology is capable of measuring over 40 different metals with enough sensitivity in many cases to detect concentrations in the low parts-per-billion range. It has been used to detect metals in such diverse fluids as drinking water[1], wine[2], sediment[3], and blood[4]. An excellent summary of the technology can be found in *Stripping Analysis: Principles, Instrumentation and Applications*[5].

2. Technology Description

2.1   Description

A prototype automated laboratory trace metals analyzer was developed which is based on the electrochemical technique of PSA pioneered by D. Jagner in the early 70's. Recent advances in electronics now enable the technique to perform completely automated copper, mercury, or arsenic metal analyses in about five minutes. The system (Figure 1) consists of (1) a computer; (2) custom control and data acquisition and analysis software; (3) a custom computer controlled potentiostat and data acquisition circuitry; and (4) a custom flow-through electrochemical cell module and sample handling components.

The high sensitivity of PSA can be attributed to the unique coupling effect of effective preconcentration steps and advanced measurement procedures. The electrode consists of a glassy carbon rod, on which is deposited a thin mercury film, or a thin gold disk. The electrode is exposed to the sample and a voltage potential is applied (Figure 2) the metal is reduced and forms an amalgam on the electrode. This concentration phase can last from 1 to 120 seconds depending on the amount of metal in solution. Typically for metal concentrations in the range of 1-30 µg/L a 30 second plating time is sufficient. After the concentration phase the voltage is removed and the potential of the electrode is measured. The potential drops until it reaches the characteristic value for metal oxidation. At this voltage the metal is oxidized and striped off the electrode. The potential remains constant until all the metal is oxidized producing a plateau in the voltage verses time graph (Figure 3). The width of the plateau is proportional to the concentration of a specific trace metal originally in solution.

Figure 1. The Trace Metals Analyzer is composed of a computer and electronic boards (on the left and a wet chemistry section (on the right).
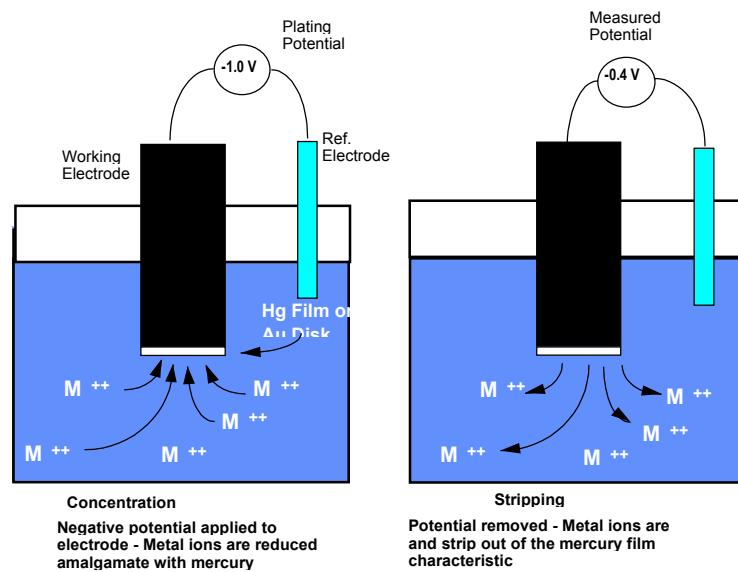

Figure 2. Potentiometric Stripping of Trace Metals is a two step process consisting of a concentration step where the metal ions are amalgamated on the electrode and a stripping step where the metals are removed.

Potentiometric Stripping Curve
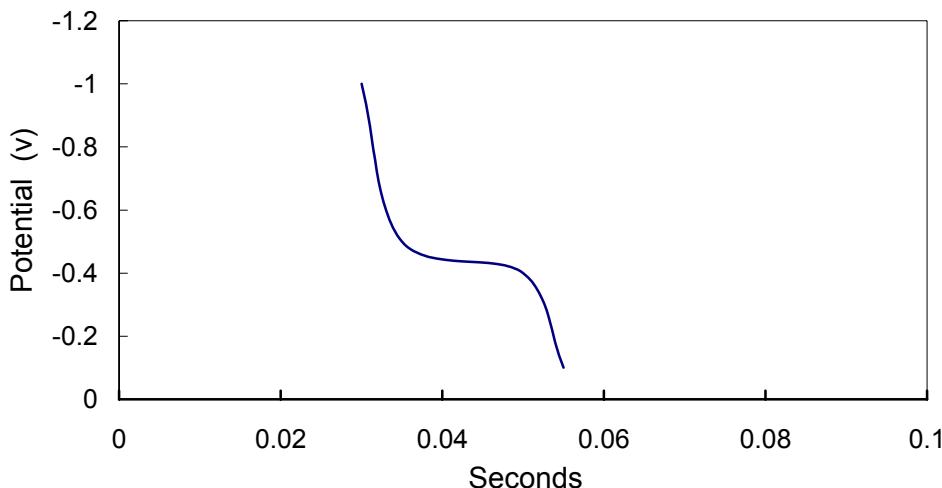
Figure 3. A potentiometric Stripping Curve. While a metal is oxidizing and stripping off of the electrode the potential remains constant. The width of this plateau is proportional to the original concentration of metal ion in solution.

To calculate the true concentration of the metal a multi-point standard curve is generated by adding known quantities of metal to the test sample and repeating the measurement. This entire process is totally automated and proceeds without any intervention. When the concentration of metal has been determined (usually in less than 5 minutes) the instrument displays and logs the concentration and the relevant measurement statistics, pumps out the test sample, rinses the cell and waits for operator command.

2.2   Strengths, Advantages and Weaknesses

The strengths of the PSA method, which is used by the ATMA, are accuracy, sensitivity, versatility, and simplicity. Increasing the concentration or plating phase of PSA allows the instrument, in many cases, to measure metal concentrations in the single digit µg/L range. Although, at these low levels representative sampling becomes such a dominant factor that field use becomes impractical. The instrument is very versatile allowing the user to operate the instrument in single sample mode or on in multiple runs on a single sample.

As will all trace metal measurement techniques the major weakness is in metal matrix effects interfering with the measurement. Interference for metal measurements include high concentrations of organics, solids, or in some cases other metals. In samples containing interferents a greatly reduced signal, greater than 10 fold, will result. Thus samples which the makeup, or potential make up, is not known, at least within an order of magnitude, should not be run with out initial confirmation using standard analysis.

2.3 Factors Influencing Cost and Performance

There are three factors that influence the cost and performance of the ATMA. These are the startup capital equipment costs, Operation and Maintenance cost and the demobilization cost. The capital equipment costs will vary depending on the useful life of the equipment. The operation and maintenance cost is mainly dependent on the cost of labor as the material maintenance costs are minimal. The demobilization costs are minimal as there are no hazardous materials associated with the instrument.

3. Site/Facility Description

3.1 Background

Two locations were selected for this demonstration. The sites were selected in consultation with Myron Anderson, USAF Wastewater Systems Program Manager, Headquarters Air Force Civil Engineering Support Agency and Katherine Ford and Nick Stencil, Pollution Prevention Technical Development Branch Code 421 at the Naval Facilities Engineering Service Center, Port Hueneme, CA. Site selection criteria included a high volume output of waste containing the demonstration metals, a permit allowing discharge of the demonstrated metals, on site treatment capability of the demonstration metals and availability and willingness of Industrial Wastewater Treatment Plant (IWTP) personnel to test this new method.

Several meetings were held with IWTP personnel to discuss the test plan. From these discussions it was found that of the various sources processed by the IWTP only the plating bath waste was routinely measured for the metals addressed by this demonstration. Plating bath waste is relatively consistent pollution source as all DoD plating shops follow military specifications when conducting plating operations.

The sites selected were the IWTPs located at North Island Naval Air Station and the Puget Sound Naval Shipyard. The North Island IWTP uses a conventional batch treatment process while the Puget Sound IWTP is demonstrating the advanced Molecular Recognition Technology system.

3.2 Site/Facility Descriptions

3.2.1 North Island Naval Air Station IWTP. The IWTP is located on the western end of the North Island Naval Air Station. It is operated by the Navy Public Works Center, Code 932. Processes contributing wastewater to this facility include: batch treatment of hauled wastewater, oil/water separation, paint stripping, steam cleaning, film processing, vehicle and aircraft washing, and cooling tower bleed. The total flow through this facility is approximately 184,000 gpd. This demonstration will concentrate on plating bath wastewater.

At the IWTP, plating bath wastewater arrives by bulk carrier and is placed in storage tanks. Samples are collected from the tanks and analyzed for metals at an off-site laboratory. Based on this analysis a treatment plan is developed. A small volume of the waste (~600 ml) is treated in the IWTP field laboratory and the treated sample is tested, at the off-site analytical laboratory, to assess the effectiveness of the treatment process. If the resultant metal levels are below discharge permit levels (Table 1) the treatment process is scaled up and used to treat the bulk waste. The bulk waste is treated then discharged into the San Diego municipal sewage system without further measurement.

Table 1. Metal discharge limits for the North Island Naval Air Station IWTP	
Metal	Maximum Concentration (mg/l)
Arsenic	0.8
Chromium	2.8
Copper	1.8
Mercury	0.8
Selenium	0.8

3.2.2 Puget Sound Naval Shipyard IWTP. The Puget Sound Naval Shipyard is engaged in extensive maintenance work on small and large Naval vessels. The work is heavy industrial and includes several metal plating and cleaning operations such as etching, passivating, plating, galvanizing and general cleaning. Many of these processes generate rinse water that must be processed before discharge.

In 1976, the PSNSY constructed an Industrial Waste Pretreatment Facility (Building 871) to treat industrial wastes from several facilities throughout the Shipyard. Building 871 is located on the north end of the Shipyard facility and is part of the Public Works Department, operated by Code 910HZ. The waste treatment facility was built in a central location the shipyard with piping to transfer the wastewater. Today the only piping remaining is from the largest generator of wastewater, the Metal Preparation Facility. The IWTP still receives waste by tank delivery in minimal quantities from the sheet metal shop and the photo laboratory.

The building containing the treatment plant was design to process wastewater in a two level heavy concrete structure. The upper level covers a floor area of approximately 9,000 sq. ft. It is housed in a prefabricated metal structure with masonry walls on the east and south sides. All process equipment is located within the building, and only external activity is unloading of the wastewater from portable tanks and process chemicals, and loading of sludge to be hauled to the Hazardous Waste Containing Storage Area in Building 944.

The PSNSY IWTP has a RCRA to operate under "permit by rule" exempting it from requiring a Part B Permit. It now functions under the regulations of the Clean Water Act. Treated wastewater is discharged to the Shipyard sanitary sewerline, and eventually discharged to the City of Bremerton's sanitary sewer plant. Sludge is dewatered, drummed, and transported to Building 944 then disposed as a RCRA listed hazardous waste and an off-site, permitted Treatment, Storage and Disposal Facility.

The MRT system designed for the ESTCP demonstration is intended to recover those metals found in the miscellaneous tank at PSNSY's IWTP. The waste stream from the miscellaneous tank has the range of metal ions shown in Table 2. The metal contaminants vary with in this range depending on the metal finishing activities of the Metal Preparation Facility ant the time of analysis.

Table 2. Baseline Metal Concentration Range for PSNSY IWPT

Metal	Baseline Influent Range (mg/l)
Zinc	1.12-10.8
Lead	0.10-1.99
Copper	3.66-17.2
Silver	0.11-0.38
Cadmium	0.13-2.16
Nickel	1.15-7.93
Chromium (total)	2.20-18.5

4. Demonstration Approach

4.1 North Island Naval Air Station Waste Water Treatment Plant

4.1.1 Performance Objectives. At the North Island Naval Air Station Waste Water Treatment Plant when a plating bath waste load arrives, usually by bulk carrier, samples are collected and taken to the plant laboratory. In the laboratory a process plan to treat the waste is developed and tested. Analyzing the results of these small-scale treatment processes is the limiting step in large-scale treatment. Currently off-site laboratory tests are used to determine the level of contamination that remains after small-scale treatment. Often, there is a three-day turn around time for the results. If the resulting levels are too high the treatment process is adjusted and a new sample is sent to the laboratory.

This demonstration will compare the results between the ATMA, and standard laboratory analysis. The main performance objective of this demonstration is to achieve chromium, mercury and arsenic measurements equivalent in accuracy and precision to the standard laboratory test currently used without requiring a higher technical skill level with results immediately available in the field at a lower cost.

4.1.2 Physical Setup and Operation. The IWTP chemical technician at the plant laboratory will use the ATMA and the standardized laboratory test will be conducted at a certified independent testing laboratory.

4.1.3 Sampling Procedures. When a waste load arrives, usually by bulk carrier, samples before and after small-scale treatment will be collected and split. Half of each split will be taken to the plant laboratory and immediately measured by a wastewater treatment plant technician. Samples that will be stored or shipped for later analysis will be preserved. Holding time will not exceed seven days. Arsenic samples will be preserved by adding 0.5% high-purity HCl to a pH <2 in a metal free floropolymer container. Chromium samples will be preserved in a 50% NaOH solution in metal free polypropylene containers. Mercury samples will be preserved by adding 0.5% high-purity HCl or 0.5% BrCl to a pH <2 in an metal free floropolymer container.

4.1.4 Analytical Procedures. Chromium and Arsenic will be analyzed using EPA Method 200.8; Mercury will be analyzed using EPA Method 7470. Equipment blanks, field blanks, and field duplicates will be used in accordance with the QA/QC plan. Chain of custody, shipping and holding times will follow the QA/QC plan.

4.2 Puget Sound Naval Shipyard MRT Waste Water Treatment Plant

4.2.1 Performance Objectives. The performance objective of this demonstration is to show the feasibility of using the ATMA to monitor outflow of the MRT system and allow operators to easily determine, in real time, when filter breakthrough occurs. To meet that objective the

ATMA must be able to monitor the copper concentrations at a rate of 5 samples per hour for concentrations ranging from 10-100 µg/l.

4.2.2 Physical Setup and Operation. The ATMA was connected to sampling port 6 of the MRT system. The ATMA was run during the Acid/Alkali MRT mixed bed column flow tests. In these these tests column 1 and column 2 are connected in series and the copper concentration exiting column 2 will be measured. The ATMA was used by the MRT operators to determine when filter breakout occurs. The ATMA was operated in a continuous mode at a frequency of not less than 5 samples per hour.
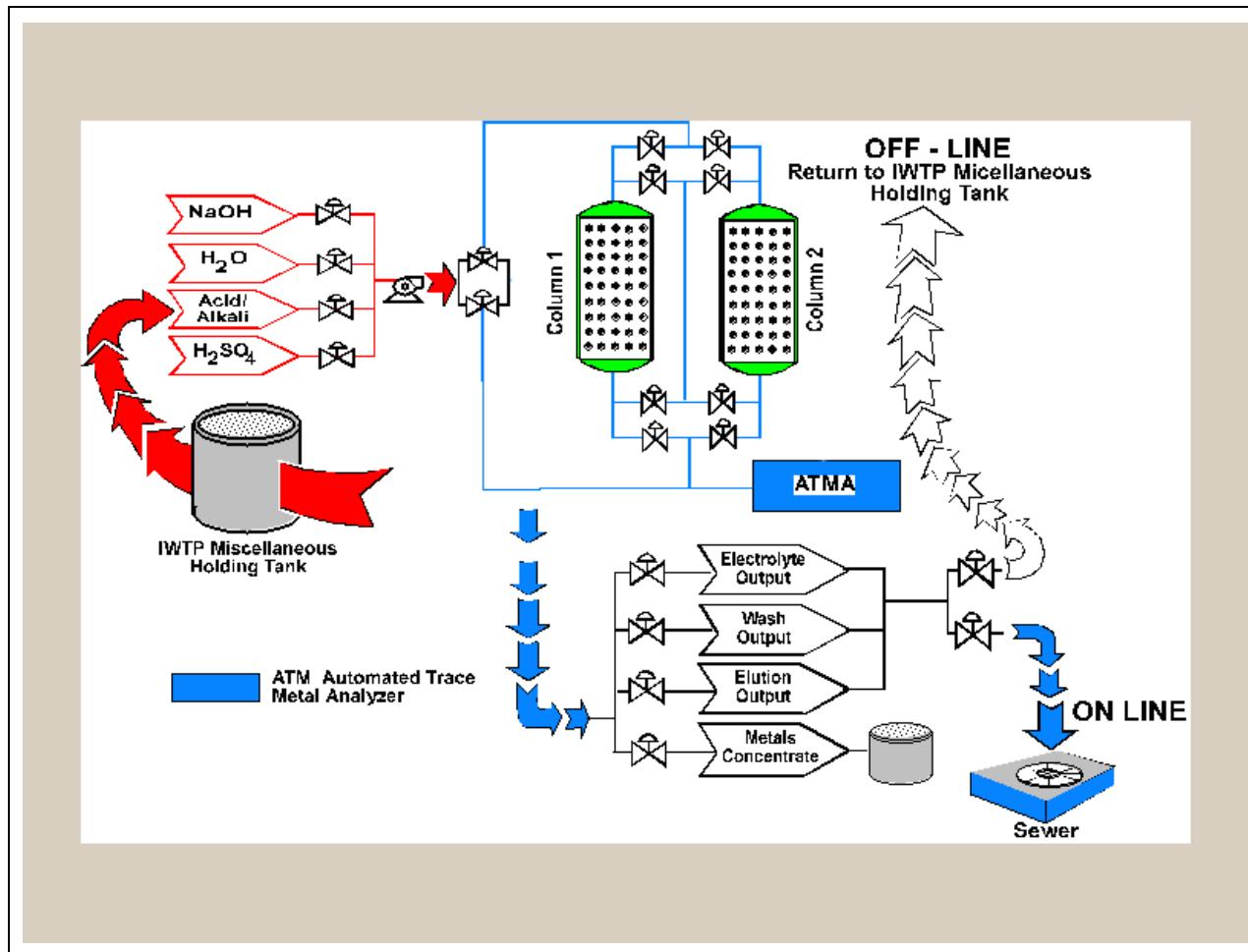

Figure 4. The ATMA is located at port 6. It measures copper ion concentrations in the effluent after the effluent has passed through the MRT columns.

4.2.3 Sampling Procedures. There were two demonstration runs using the ATMA. In the first run, samples will be collected every thirty minutes in pre-cleaned trace metal free polyethylene bottles and immediately hand carried to the Shipyard analytical laboratory for analysis. The ATMA was operating in a continuous mode at a rate of one sample every thirty minutes. The time and amount of waste processed was noted on the ATMA log and sample bottles.

The second run demonstrated the ability of the ATMA to continuously monitor and plot metal concentrations in real-time. The operators used he concentrations to determine, in real-time, when the exact moment breakout of the filter bed occurred.

4.2.4 **Analytical Procedures.** Copper was analyzed using EPA Method 200.8 Equipment blanks, field blanks, and field duplicates were used in accordance with the MRT QA/QC plan.

5. Performance Assessment

5.1 Performance Data

A series of laboratory tests were conducted to assess the performance of the ATMA in measuring arsenic, chromium, copper, mercury and selenium. Three tests were performed on each metal to determine interferences, linearity and sensitivity response.

To determine the metal ion interferences a study was conducted to assess the performance of the ATMA in the presence of 15 different metal ions at high and low concentrations. A decrease in instrument sensitivity greater than 50% was considered significant enough to impair the metal measurement.

Linearity was tested by measuring a range of known metal concentrations. The initial metal concentrations in the prepared base stock samples were determined using an ICP-MS. The base stock sample was then diluted to the required metal concentration using ultra-clean trace-metal-free water.

 Placing the ATMA in an automated mode and repeatedly measuring a single sample allowed the observation of the change in sensitivity of the instrument over time. Ten measurements were taken and the relative standard deviation was calculated.

The ATMA performs standard addition calibrations after each measurement and calculates the concentration of the measured metal based on these calibrations. To accurately measure the interferences, linearity and sensitivity the raw analog to digital converter output was used. This allows examination of the performance before the ATMA automatically adjusts for any changes in sensitivity or linearity.

5.11 Arsenic. In Table 3 it can be seen that all 15 metals at 635 µg/l and 1250 µl/l significantly suppress the sensitivity of the ATMA to arsenic. Given this performance, arsenic should only be measured using relatively clean well-defined samples such as drinking or relatively clean well water.

As seen in Figures 5 and 6 the arsenic response of the ATMA was linear with a $R^2 > 0.95$ for concentrations ranging from 0-368 µg/l.

Figure 7 shows a relative standard deviation of 9.2% over 10 runs. This is caused by a linear decrease in instrument sensitivity most likely due to degradation of the working electrode. Polishing the electrode restores it's sensitivity. Using this data it is estimated that the electrode would require polishing after a 50% decrease in sensitivity or after approximately every 54 measurements.

Table 3. Arsenic interference study of 15 metals at 635 µg/l and 1250 µg/l. The original water sample was spiked with arsenic(III) to 32 µg/l and split three ways for each metal tested. Aliquots two and three were spiked, with the interfering ion, to 635 µg/l and 1250 µg/l respectively. The percent change in measured arsenic levels between the spiked samples and the original 32 µg/l sample was recorded.

| Arsenic Interference (32 µg/l conc.)			
Interfering Ion	635 µg/l Interfering Ion Added	1250 µg/l Interfering Ion Added	Interference
	% change in instrument sensitivity	% change in instrument sensitivity	< 50% decrease in sensitivity
Aluminum(III)	92.5	87.6	Yes
Antimony(III)	82.3	63.4	Yes
Bismuth(III)	< 100	< 100	Yes
Cadmium(II)	< 100	< 100	Yes
Copper(II)	< 100	< 100	Yes
Chromium(VI)	< 100	< 100	Yes
Iron(III)	85.4	69.7	Yes
Lead(II)	100.0	100.0	Yes
Magnesium(II)	94.0	87.6	Yes
Manganese(II)	89.7	8305	Yes
Mercury(II)	< 100	< 100	Yes
Nickel(II)	95.7	83.5	Yes
Selenium(IV)	< 100	< 100	Yes
Tin(IV)	86.9	72.7	Yes
Zinc(II)	95.5	91.1	Yes
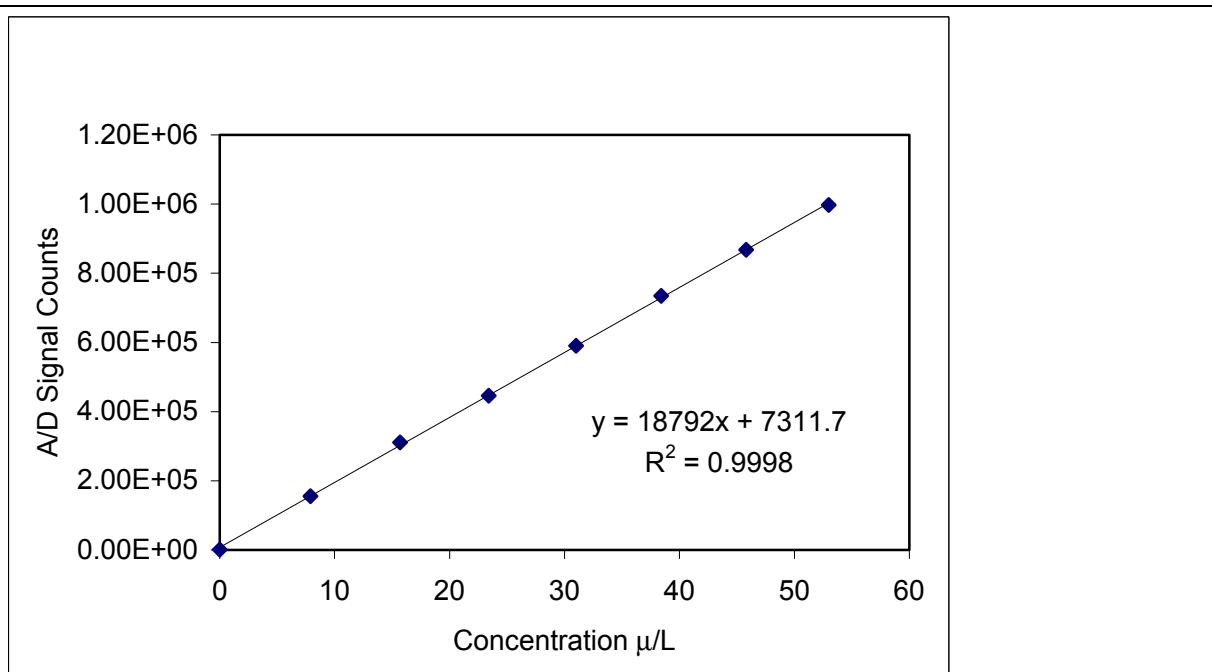
Figure 5. Response of the ATMA to water samples spiked wit 0-53μg/l Arsenic(III)
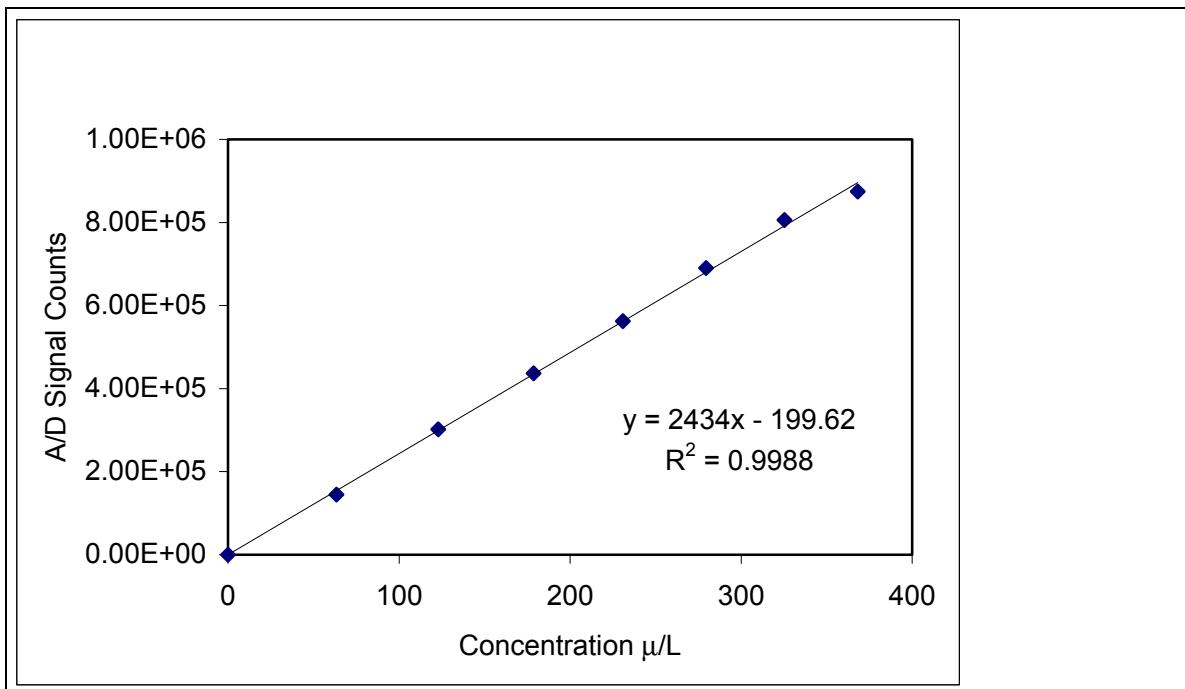
Figure 6. Response of the ATMA to water samples spiked wit 63-368μg/l Arsenic(III)
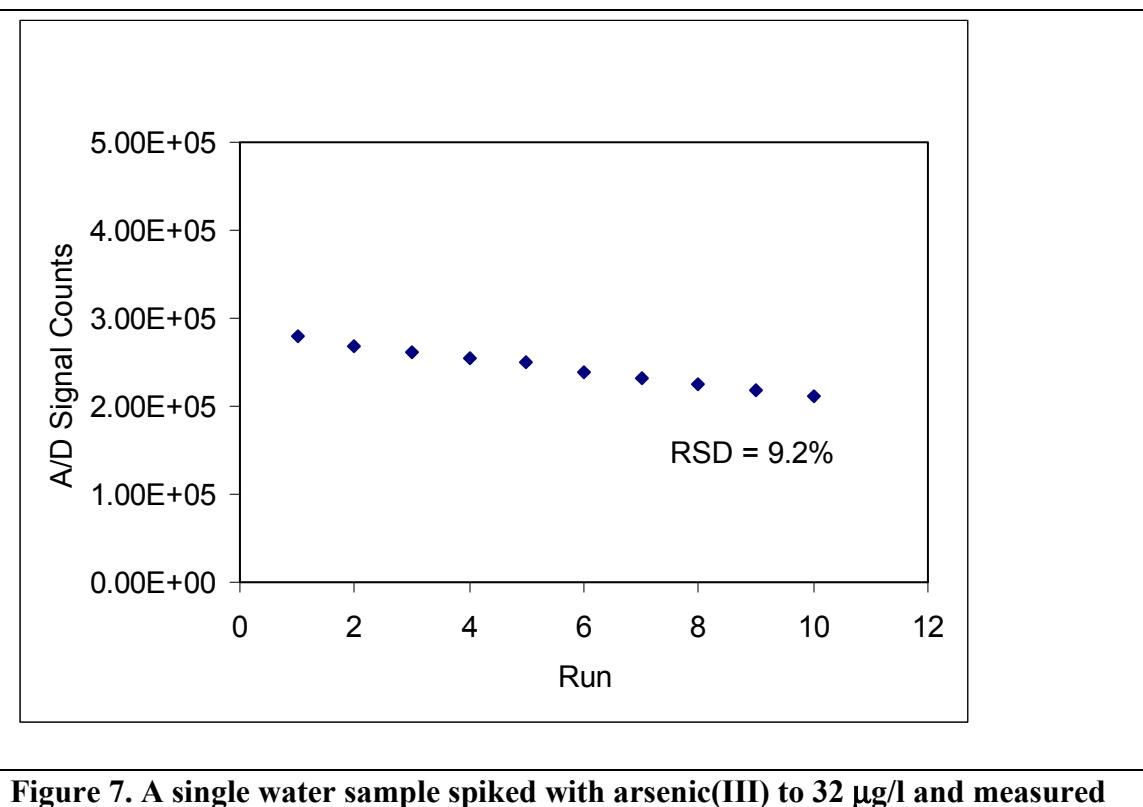
Figure 7. A single water sample spiked with arsenic(III) to 32 μg/l and measured 10 times. The relative standard deviation for this set is 9.2%

5.12 Chromium. In Table 4 it can be seen that of the 15 metals tested two, antimony(III) and iron(III) interfered with chromium measurements. Both occurred at the 1490 μg/l level. It is recommended that test samples known to contain iron(II) or antimony(III) be tested before using the ATMA for monitoring.

As seen in Figures 8 and 9 the chromium response of the ATMA was linear with a R^2>0.95 for concentrations ranging from 0-65 μg/l. Beyond 65 μg/l the electrode became saturated and rapidly lost linearity.

Figure 10 shows a relative standard deviation of 3.1% over ten runs. No decrease in sensitivity was observed during the runs.

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Table 4. Chromium interference study of 15 metals at 625 μg/l and 1490 μg/l. The original water sample was spiked with chromium(VI) to 16 μg/l and split three ways for each metal tested. Aliquots two and three were spiked, with the interfering ion, to 625 μg/l and 1490 μg/l respectively. The percent change in measured chromium levels between the spiked samples and the original 16 μg/l sample was recorded.

| Chromium Interference (16 μg/L conc.)			
Interfering Ion	624 μg/L Interfering Ion Added	1490 μg/L Interfering Ion Added	Interference
	% change in instrument sensitivity	% change in instrument sensitivity	< 50% decrease in sensitivity
Aluminum(III)	15.4	17.9	No
Antimony(III)	41.5	62.3	Yes
Arsenic(III)	14.1	27.7	No
Bismuth(III)	4.0	39.1	No
Cadmium(II)	13.5	17.0	No
Copper(II)	25.2	3.5	No
Iron(III)	13.3	74.3	Yes
Lead(II)	18.1	16.5	No
Magnesium(II)	25.4	6.4	No
Manganese(II)	13.3	19.9	No
Mercury(II)	25.4	11.8	No
Nickel(II)	13.2	16.0	No
Selenium (IV)	13.1	17.8	No
Tin(IV)	20.9	20.2	No
Zinc(II)	8.6	28.1	No
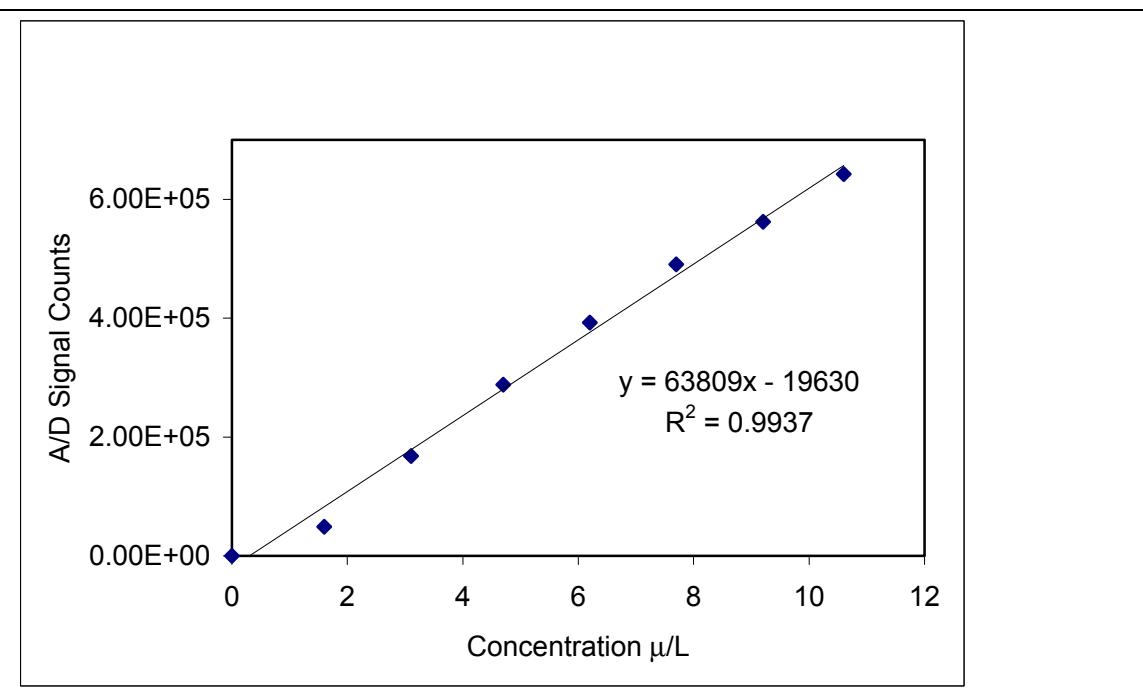
Figure 8. Response of the ATMA to water samples spiked wit 0-11µg/l chromium(VI).
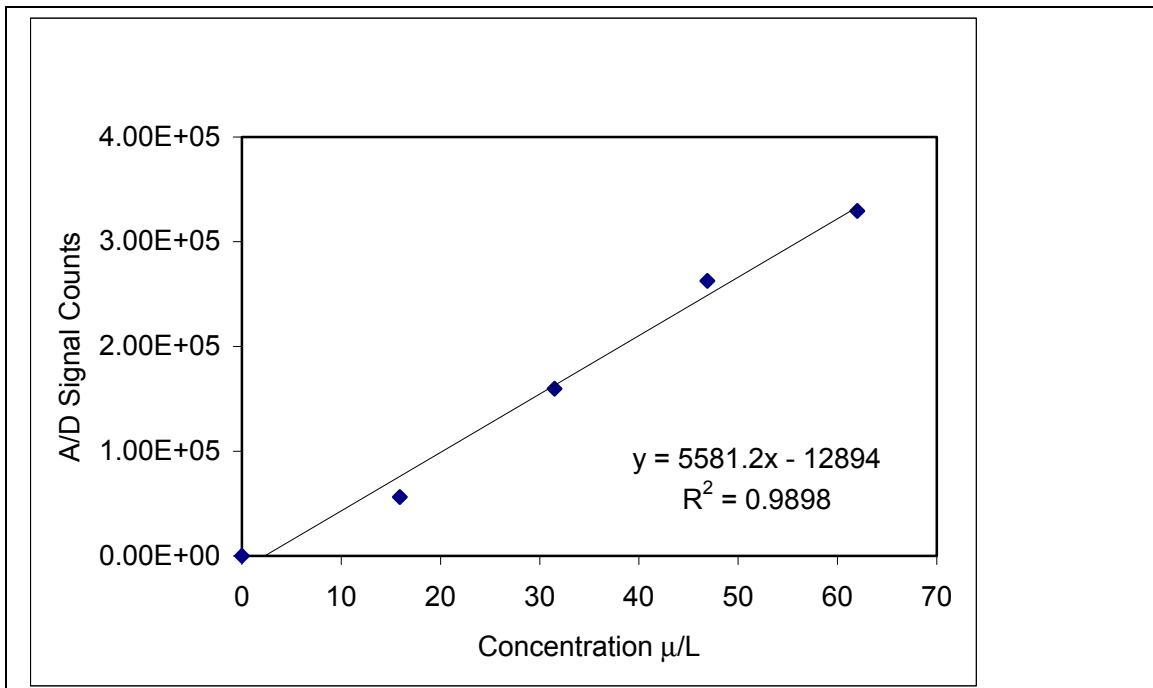
Figure 9. Response of the ATMA to water samples spiked wit 15-65µg/l chromium(VI).
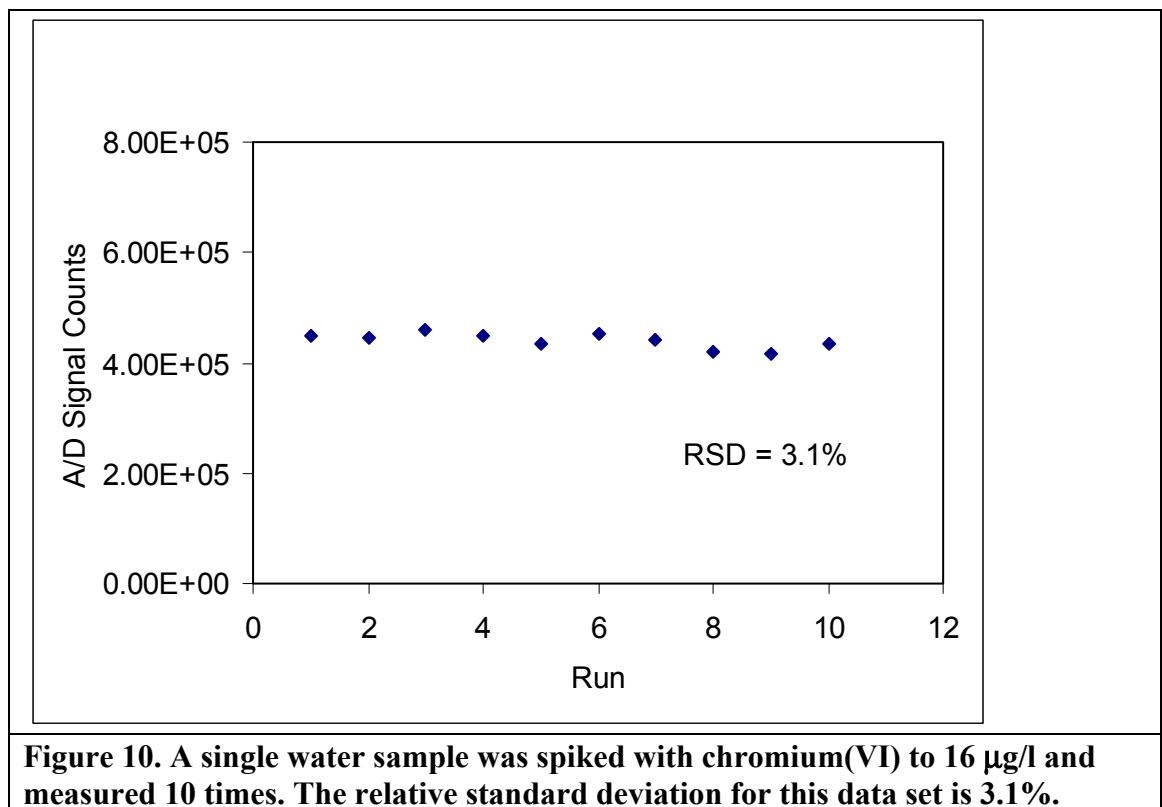
Figure 10. A single water sample was spiked with chromium(VI) to 16 μg/l and measured 10 times. The relative standard deviation for this data set is 3.1%.

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5.13 Copper. In Table 5 it can be seen that of the 15 metals tested that 9 interfered with copper measurements at the 635 μg/L level. At the 2979 μg/L level there were 10 interferents. When measuring copper with the ATMA the concentration of the interfering metal ions should be checked beforehand.

As seen in Figures 11 and 12 the copper response of the ATMA was linear with a R^2>0.99 for concentrations ranging up to 225 μg/L.

Copper measurements show excellent linearity. The relative standard deviation (Figure 13) from measuring a sample 10 times was less than 2%.

Table 5. Copper interference study of 15 metals at 635 μg/l and 2979 μg/l. The original water sample was spiked with copper(II) to 32 μg/l and split three ways for each metal tested. Aliquots two and three were spiked, with the interfering ion, to 635 μg/l and 2979 μg/l respectively. The percent change in measured chromium levels between the spiked samples and the original 32 μg/l sample was recorded.

Copper Interference (32 μg/L conc.)			
Interfering Ion	635 μg/L Interfering Ion Added	2979 μg/L Interfering Ion Added	Interference
	% change in instrument sensitivity	% change in instrument sensitivity	< 50% decrease in sensitivity

Aluminum(III)	19.8	9.0	No
Antimony(III)	55.5	90.8	Yes
Arsenic(III)	78.0	88.2	No
Bismuth(III)	68.5	75.1	Yes
Cadmium(II)	20.0	13.7	No
Copper(II)			
Chromium(VI)	15.4	14.3	No
Iron(III)	12.7	13.0	No
Lead(II)	22.3	62.3	Yes
Magnesium(II)	56.7	54.3	Yes
Manganese(II)	55.0	53.9	Yes
Mercury(II)	98.8	89.6	Yes
Nickel(II)	63.0	54.8	Yes
Selenium (IV)	61.2	62.9	Yes
Tin(IV)	54.3	50.7	Yes
Zinc(II)	48.2	11.8	No
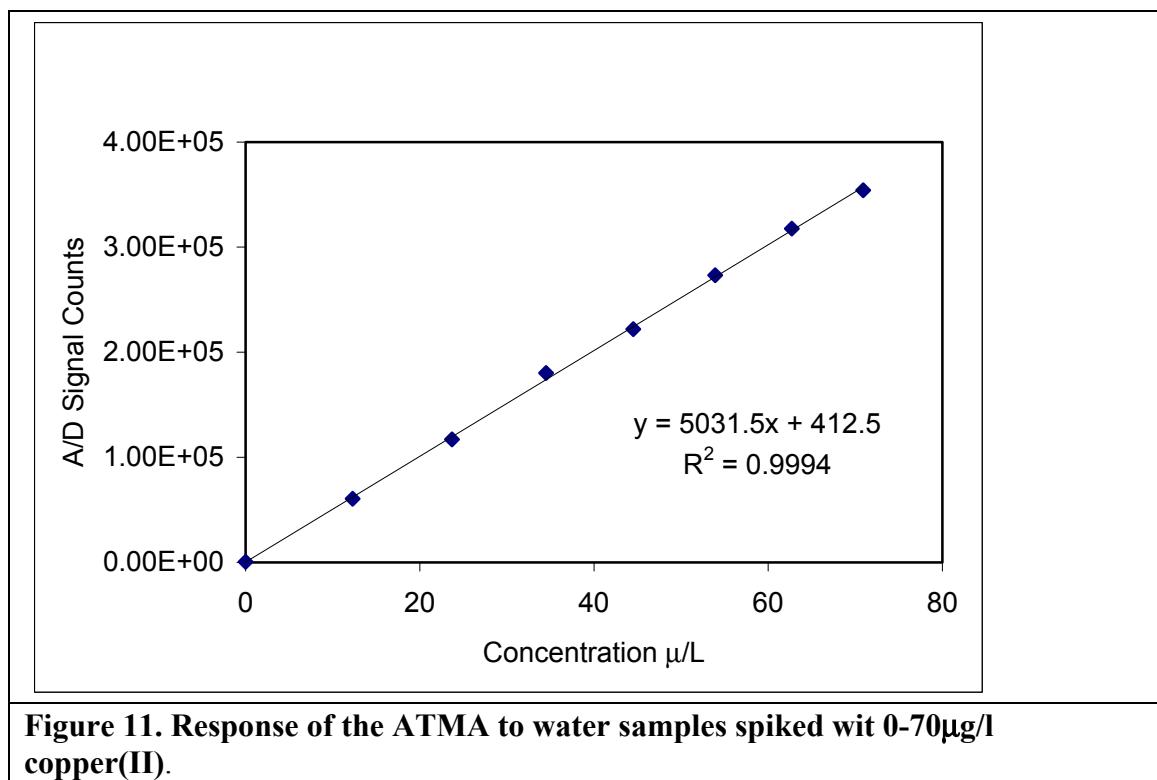
**Figure 11. Response of the ATMA to water samples spiked wit 0-70μg/l copper(II)**.
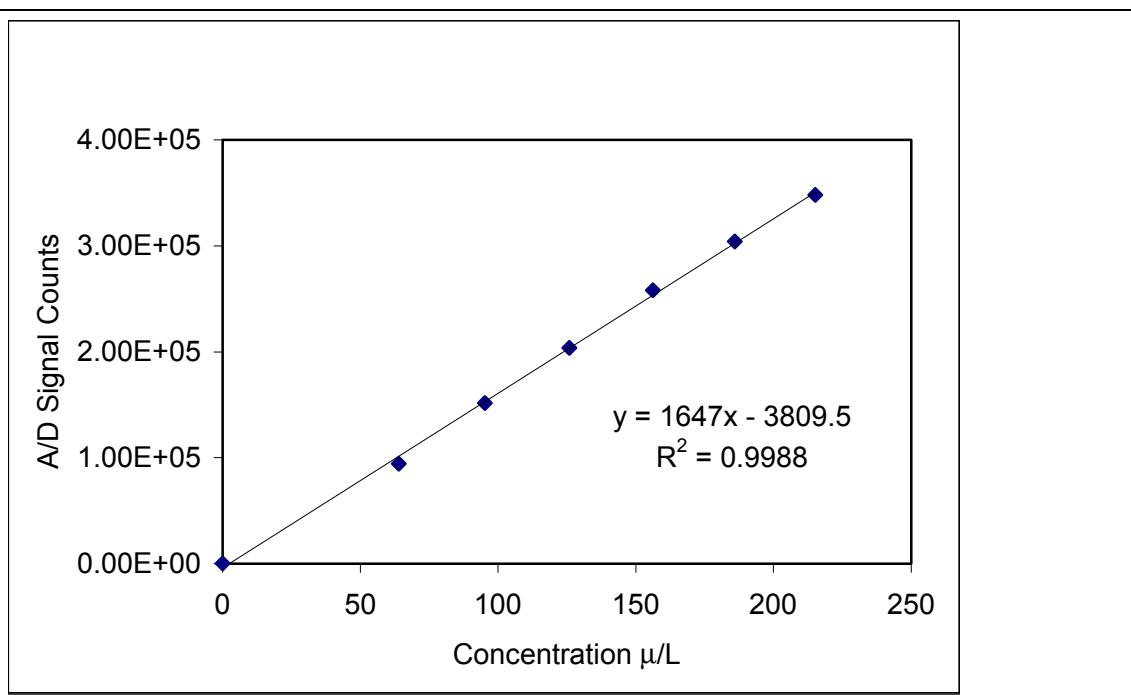
**Figure 12. Response of the ATMA to water samples spiked wit 64-215μg/l copper(II)**.
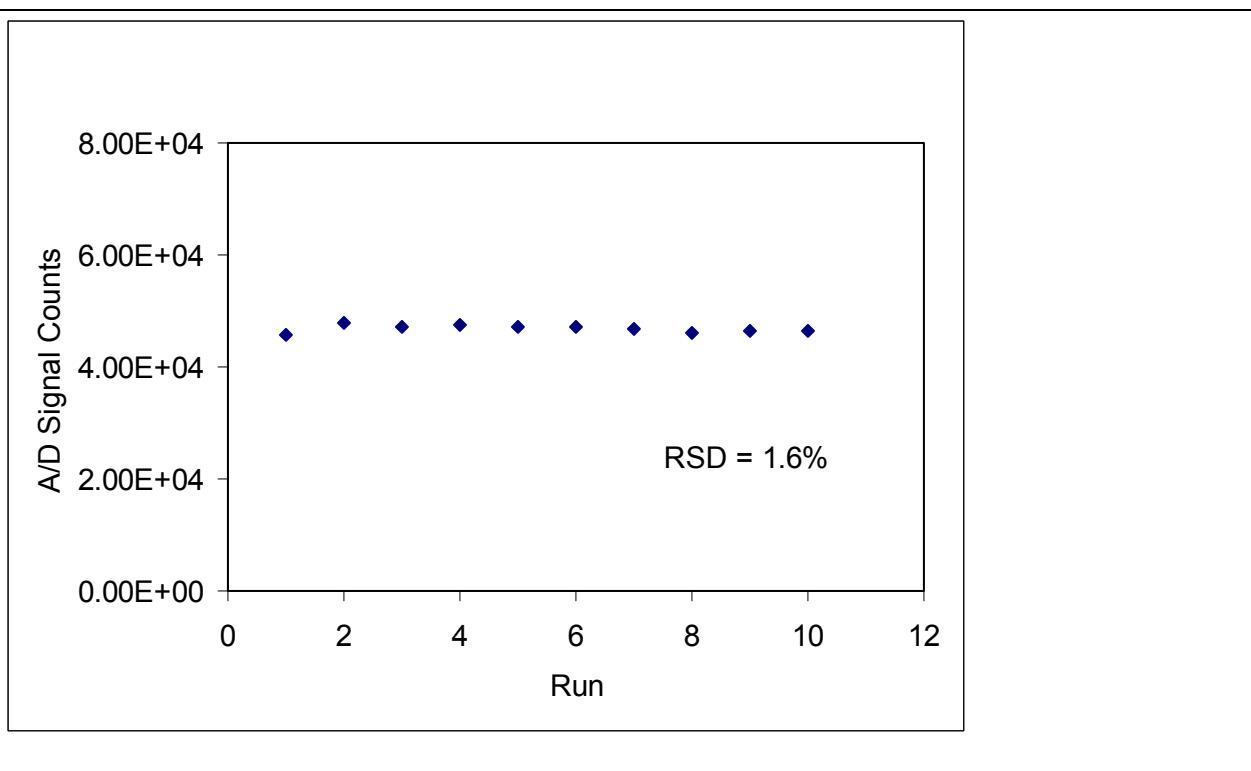
Figure 13. A single water sample was spiked with copper(II) to 32 μg/l and measured 10 times. The relative standard deviation for this set is 1.6%

5.14 Mercury. In Table 6 it can be seen that of the 15 metals tested two, bismuth(III) and selenium(IV) interfered with mercury measurements. Bismuth(III) was at the higher 2976 µg/L level and selenium(IV) was at both levels tested. It would be recommended that test samples known to contain bismuth(III) or selenium(IV) be tested before using the ATMA for monitoring.

As seen in Figure 14 and Figure 15 the response of the ATMA to mercury was linear ($R^2>0.99$) up to 400 µg/L and the linearity of multiple measurements (Figure 16) was 9.2%.

Table 6. Mercury interference study of 15 metals at 635 µg/l and 2976 µg/l. The original water sample was spiked with mercury(II) to 32 µg/l and split three ways for each metal tested. Aliquots two and three were spiked, with the interfering ion, to 635 µg/l and 2976 µg/l respectively. The percent change in measured chromium levels between the spiked samples and the original 32 µg/l sample was recorded.

Mercury Interference (32 µg/L conc.)			
Interfering Ion	635 µg/L Interfering Ion Added	2976 µg/L Interfering Ion Added	Interference
	% change in instrument sensitivity	% change in instrument sensitivity	< 50% decrease in sensitivity
Aluminum(III)	11.8	16.4	No
Antimony(III)	4.4	18.9	No
Arsenic(III)	16.0	17.0	No
Bismuth(III)	16.5	68.3	Yes
Cadmium(II)	13.1	4.2	No
Copper(II)	4.4	3.0	No
Chromium(VI)	3.5	22.5	No
Iron(III)	2.4	20.1	No
Lead(II)	0.1	13.0	No
Magnesium(II)	5.47	17.8	No
Manganese(II)	15.6	18.5	No
Nickel(II)	1.0	6.2	No
Selenium(IV)	92.8	100	Yes
Tin(IV)	3.9	8.7	No
Zinc(II)	2.4	9.9	No
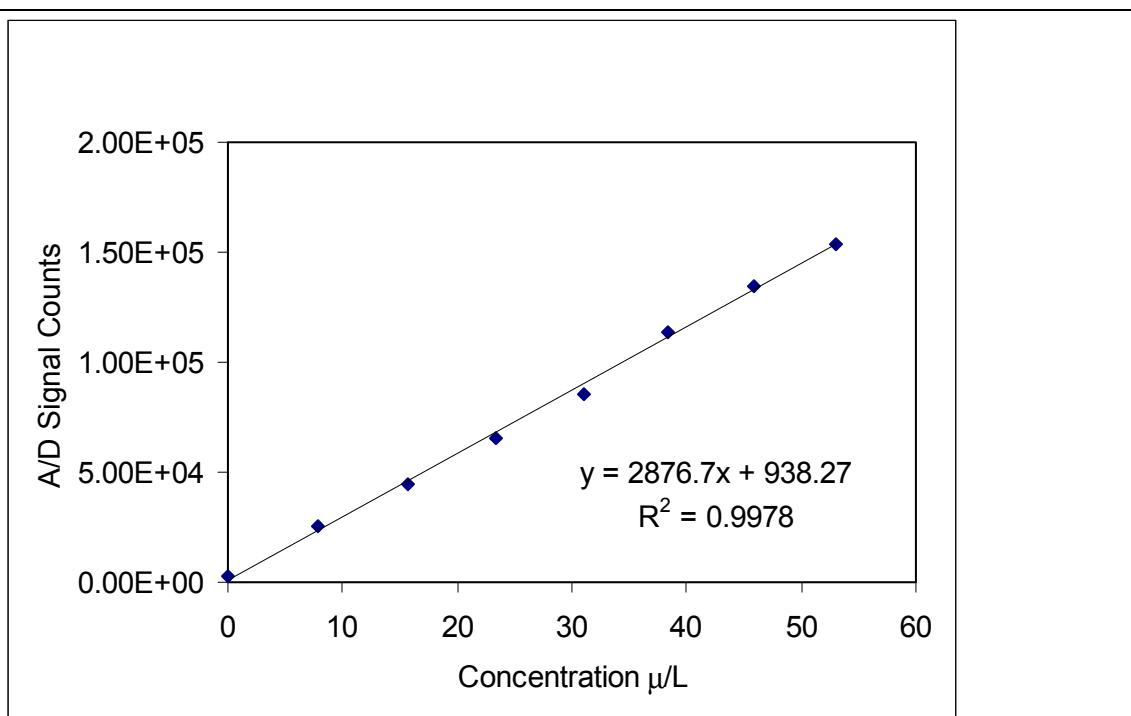
Figure 14. Response of the ATMA to water samples spiked with 0-55µg/l mercury(II).

$y = 2876.7x + 938.27$

$R^2 = 0.9978$
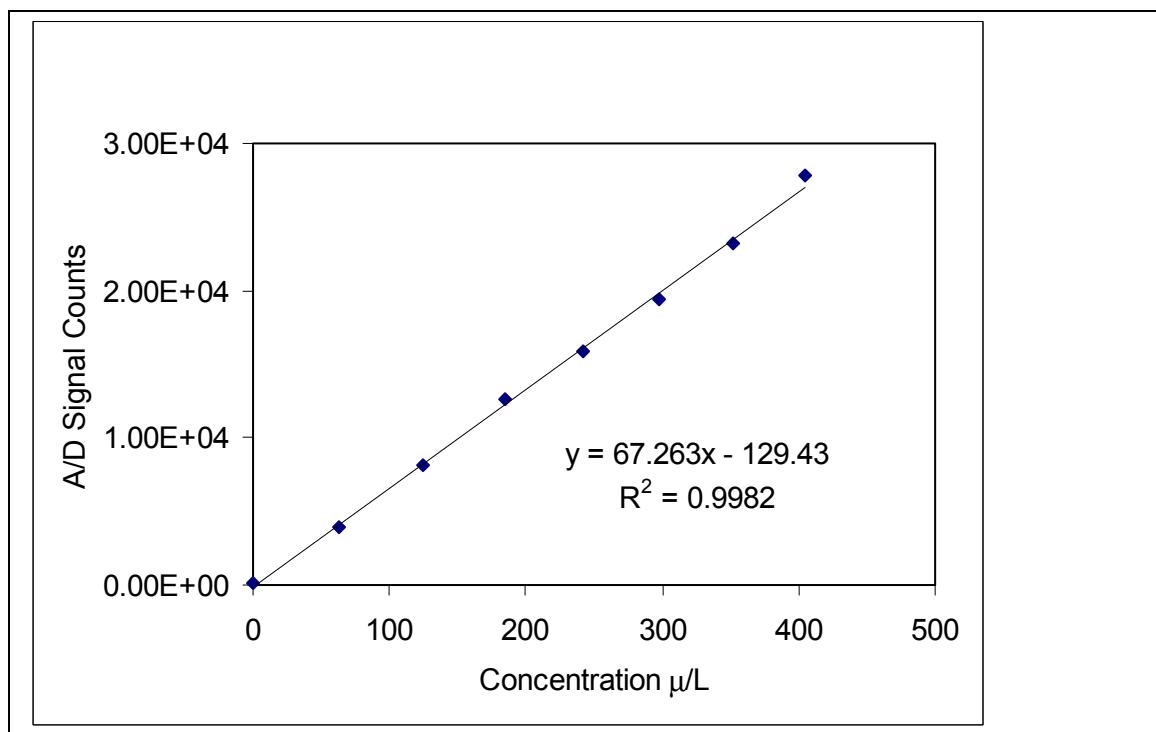
Figure 15. Response of the ATMA to water samples spiked with 60-400µg/l mercury(II).

$y = 67.263x - 129.43$

$R^2 = 0.9982$
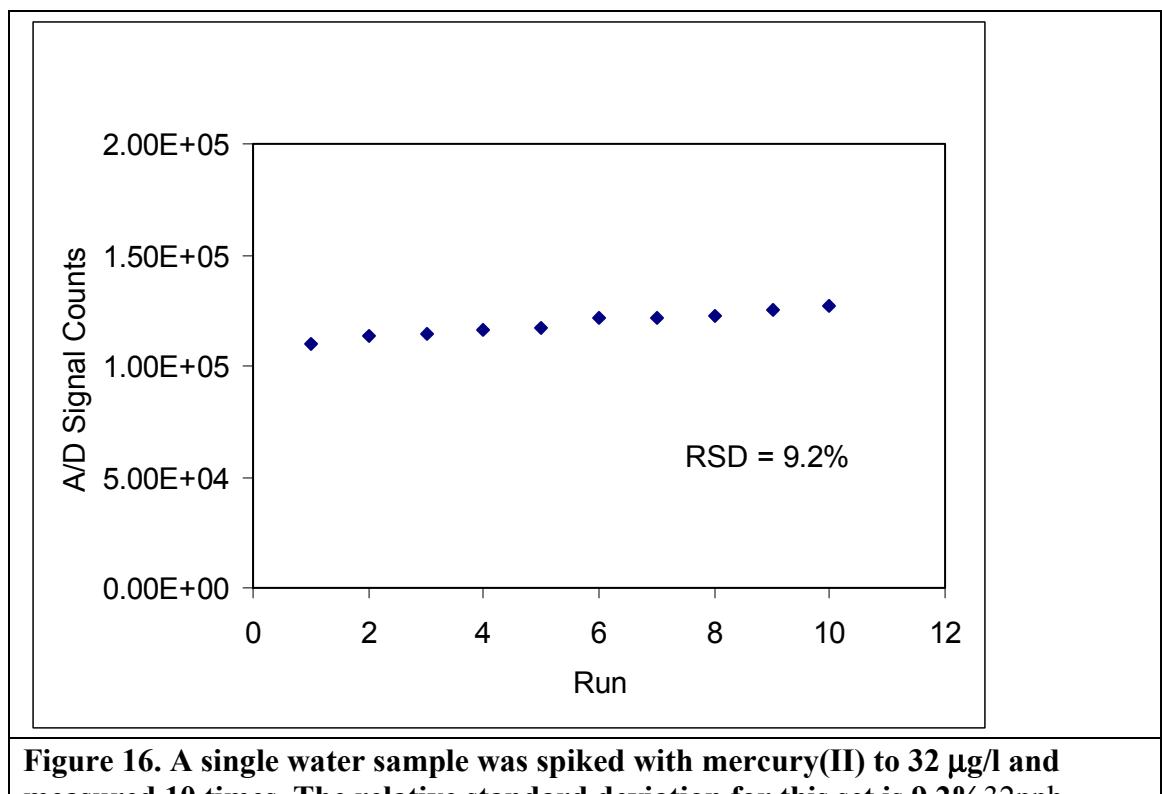
Figure 16. A single water sample was spiked with mercury(II) to 32 µg/l and measured 10 times. The relative standard deviation for this set is 9.2%32ppb

5.15 Selenium. From Table 7 it can bee see that seven of the tested ions interfered with the measurement of selenium. All these interferences occurred at the higher 2979 µg/L level. If the effluent is known to contain these high levels of metals represented samples should be analyzed before using the ATMA.

As seen in Figure 17 and Figure 18 the response of the ATMA to selenium was linear (R^2>0.99) up to 400 µg/L and the linearity of multiple measurements (Figure 19) was 4%.

Table 7. Selenium interference study of 15 metals at 635 µg/l and 2979 µg/l. The original water sample was spiked with selenium(IV) to 32 µg/l and split three ways for each metal tested. Aliquots two and three were spiked, with the interfering ion, to 635 µg/l and 2979 µg/l respectively. The percent change in measured chromium levels between the spiked samples and the original 32 µg/l sample was recorded.

Selenium Interference (32 µg/L conc.)			
Interfering Ion	635 µg/L Interfering Ion Added	2979 µg/L Interfering Ion Added	Interference
	% change in	% change in	< 50% decrease in

	instrument sensitivity	instrument sensitivity	sensitivity
Aluminum(III)	10	54	Yes
Antimony(III)	31	88	Yes
Arsenic(III)	17	43	No
Bismuth(III)	14	75	Yes
Cadmium(II)	0.1	25	No
Copper(II)	3.6	59	Yes
Chromium(VI)	28	83	Yes
Iron(III)	10	50	Yes
Lead(II)	.3	28	No
Magnesium(II)	3.5	30	No
Manganese(II)	4.1	30	No
Mercury(II)	27	100	Yes
Nickel(II)	6.8	38	No
Tin(IV)	13	59	Yes
Zinc(II)	5.4	38	No

$y = 10250x - 1230.7$

$R^2 = 0.9996$
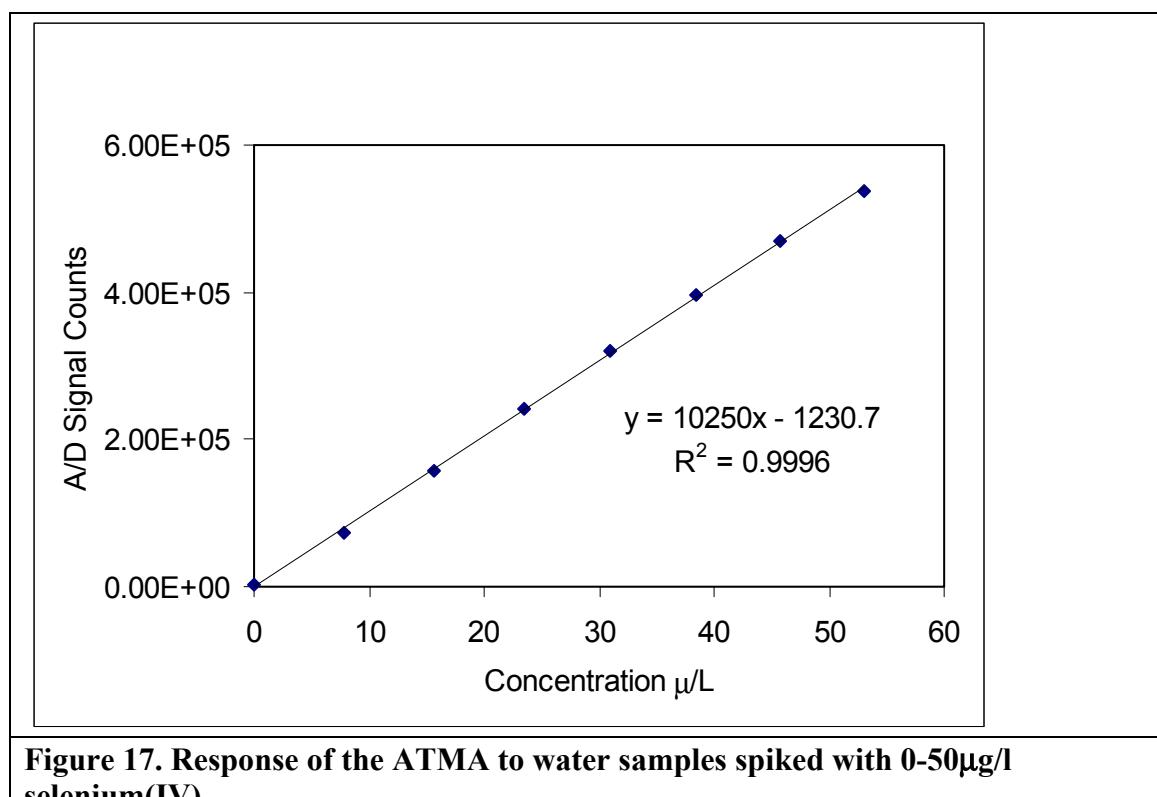
**Figure 17. Response of the ATMA to water samples spiked with 0-50μg/l selenium(IV)**.
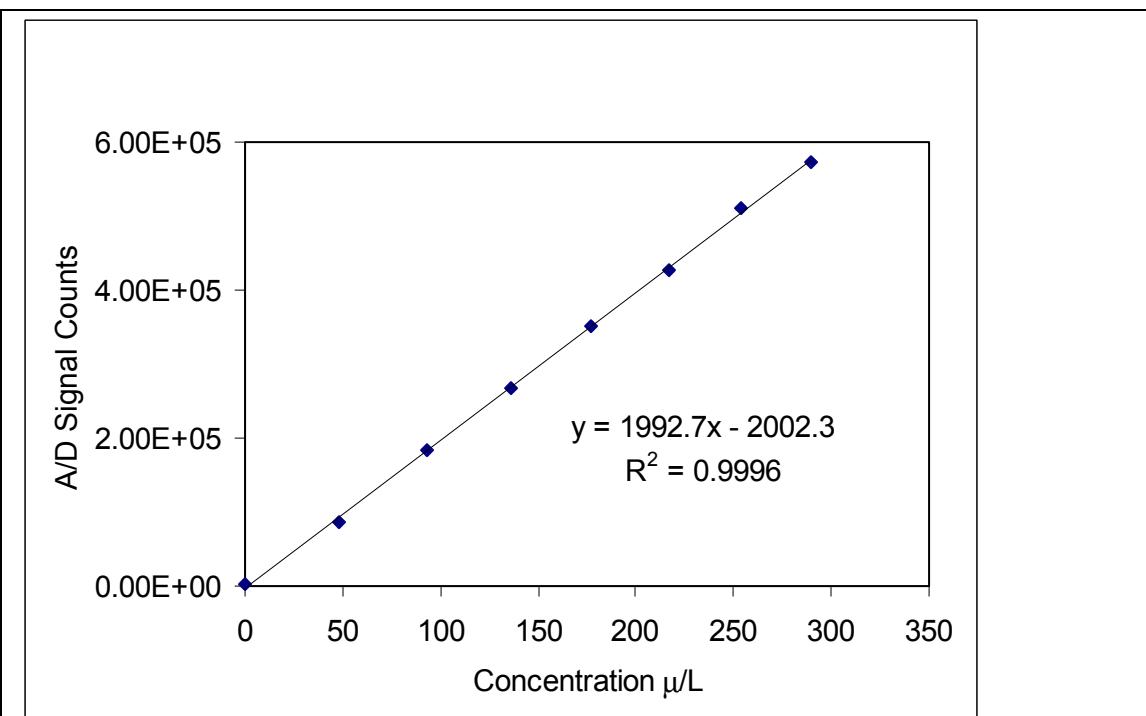
**Figure 18. Response of the ATMA to water samples spiked with 48-288μg/l selenium(IV).**
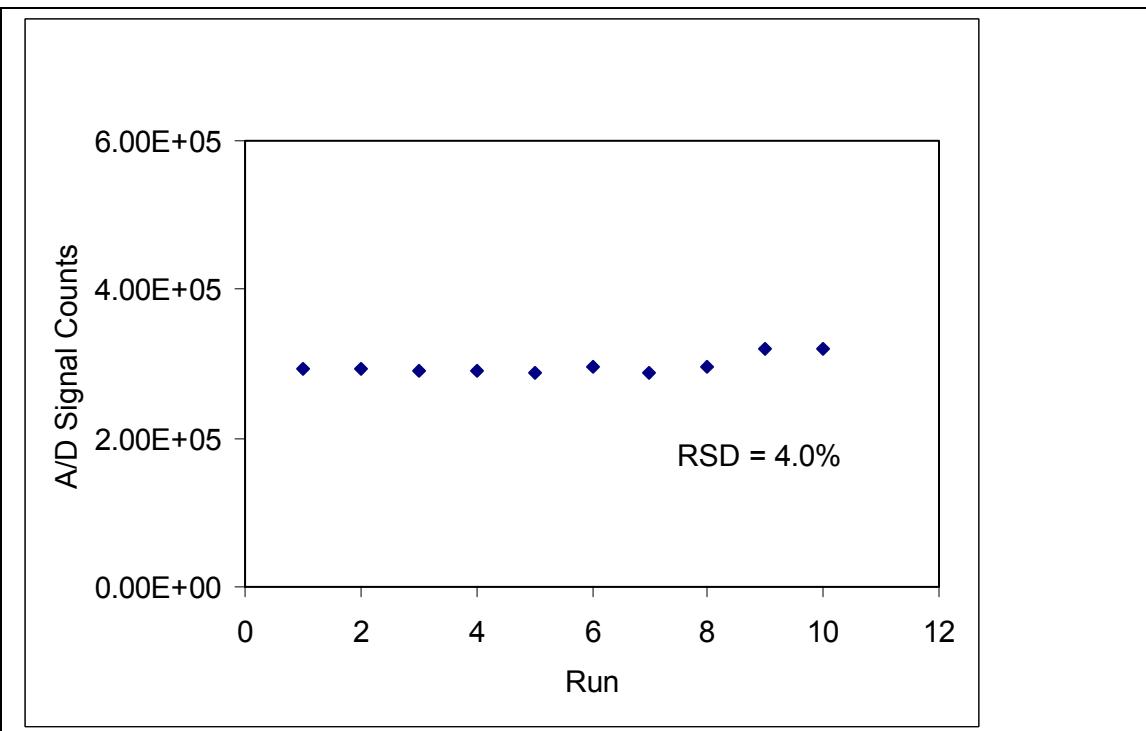
Figure 19. A single water sample was spiked with selenium(IV) to 32 μg/l and measured 10 times. The relative standard deviation for this set is 4.0%.

5.2 Data Assessment

5.2.1 North Island Naval Air Station Waste Water Treatment Plant. The ATMA was setup at the North Island Naval Air Station Waste Water Treatment Plant. Upon arrival of a bulk shipment of plating bath waste a sample was collected split and measure by the ATMA and by the standard laboratory methods as outlined in Table 8.

Table 8. Metals Tested in initial plating bath sample.

Metal	Method	Min. Det. Limit (µg/L)
Mercury	EPA7470	0.2
Arsenic	EPA1632	53
Chromium	EPA200.7	7

Both bulk samples tested did not contain any Selenium. The ATMA and the laboratory tests confirmed that Selenium was not at detectable levels. This result was expected as none of the chemicals used in the plating baths contained Selenium.

As seen in Table 9 the ATMA was unable to accurately measure the amount of trace metals in the treated or untreated plating bath waste samples. The ATMA was unable to obtain a concentration measurement for chromium due to the error of the standard addition measurements exceeding the instruments minimum linearity cutoff of $R^2=0.98$

The ATMA measurements of the treated samples were significantly below the laboratory measured concentrations. This is probably due to the tight binding of the remaining Nalco Flocculent still in solution to all or most of the metal ions. This tight binding does not allow the ATMA to measure the ion concentration.

Table 9. Waste water treatment samples from the North Island Treatment Plant. Two plating bath waste loads were tested on site. The original sample from the bulk delivery was tested at original strength and at 2X and 20X dilutions. The sample was retested after treatment with the Nalco Flocculent. The Flocculent is the waste water treatment plants method of removing metals from plating bath waste loads. Concentrations are in µg/l. The Laboratory methods used to measure the metal concentrations are listed in the Table 8.

North Island NAS Waste Water Treatment Plant Results									
		Hg		As		Cr^{total}		Cr^6	
		Lab	TMA	Lab	TMA	Lab	TMA	Lab	TMA
September Run	Sample	1050	45	310	59	927	*	ND	*
	2X dilution	525	63	155	108	463	*	ND	*
	20X dilution	56	8	17	12.7	50	*	ND	*
	Nalco Flocculent	58	13	42	ND	44	*	ND	*

October Run	Sample	766	106	240	22	926	*	ND	*
	2X dilution	383	62	120	95	463	*	ND	*
	20X dilution	41	13	13	5.8	50	*	ND	*
	Nalco Flocculent	58	ND	42	ND	44	*	ND	*

5.2.2 Puget Sound Naval Shipyard MRT Waste Water Treatment Plant. The ATMA was setup at the Puget Sound Naval Shipyard Waste Water Treatment Plant. The instrument measured the metal concentrations of the ESTCP funded Molecular Recognition Treatment (MRT) demonstration. The MRT system uses macro-cyclic chelating ligands for removal, separation and recovery of metals. By taking advantage of the high affinity and selectivity of these ligands, MRT systems can be designed to target the toxic metals found in DoD industrial influents.

These specialized ligands are bonded to polymer supports and are very stable in the solid form. This allows the ligands to be used in a packed bed or membrane configuration at the high flow rates required by typical DoD IWTPs. This demonstration used the high volume acid/alkali influent waste stream at the PSNSY industrial wastewater treatment plant. The ATMA was connected to Port 6 of the MRT system to monitor copper levels in real-time at 15 minute intervals. An initial analysis of the effluent at Port 6 is listed in Table 10. When break through of the filtration process occurs copper levels at the end of the treatment process (Port 6) rise above 40 µg/l indicating that the filter system requires maintenance.

Table 10. The results of the laboratory analysis of the effluent stream at port 6 at the start of the first demonstration run.

PSNS /MRT Composite Sample Concentrations				
Metal	Anal. Method	Prep Method	Detection Limit (ppb)	Sample Conc. (ppb)
Antimony	EPA 6010B	EPA3010A	5	6
Arsenic	EPA 6010B	EPA3010A	5	ND
Barium	EPA 6010B	EPA3010A	1	33
Beryllium	EPA 6010B	EPA3010A	1	1
Cadmium	EPA 6010B	EPA3010A	3	ND
Chromium	EPA 6010B	EPA3010A	3	44
Cobalt	EPA 6010B	EPA3010A	3	33
Lead	EPA 6010B	EPA3010A	5	ND
Mercury	EPA 6010B	EPA3010A	4	ND
Molybdenum	EPA 6010B	EPA3010A	5	15
Nickel	EPA 6010B	EPA3010A	3	6

Selenium	EPA 6010B	EPA3010A	5	8
Silver	EPA 6010B	EPA3010A	2	5
Thallium	EPA 6010B	EPA3010A	5	20
Vanadium	EPA 6010B	EPA3010A	3	ND
Zinc	EPA 6010B	EPA3010A	10	3
Total Organic C	EPA 415.1		3,000	11,000

The first demonstration run was used to compare the copper concentrations measured by the ATMA to grab samples measured in the laboratory using EPA Method 200.8. The MRT process flow was started and run past breakthrough until copper concentrations at Port 6 exceed 200 µg/l. As seen in Figure 20 excellent linearity was achieved with a $R^2 = 0.99$. However, there was a slight offset of 15 µg/l throughout the measurement range. This is most likely due to the inability of the ATMA to measure the most tightly complexed copper ions.
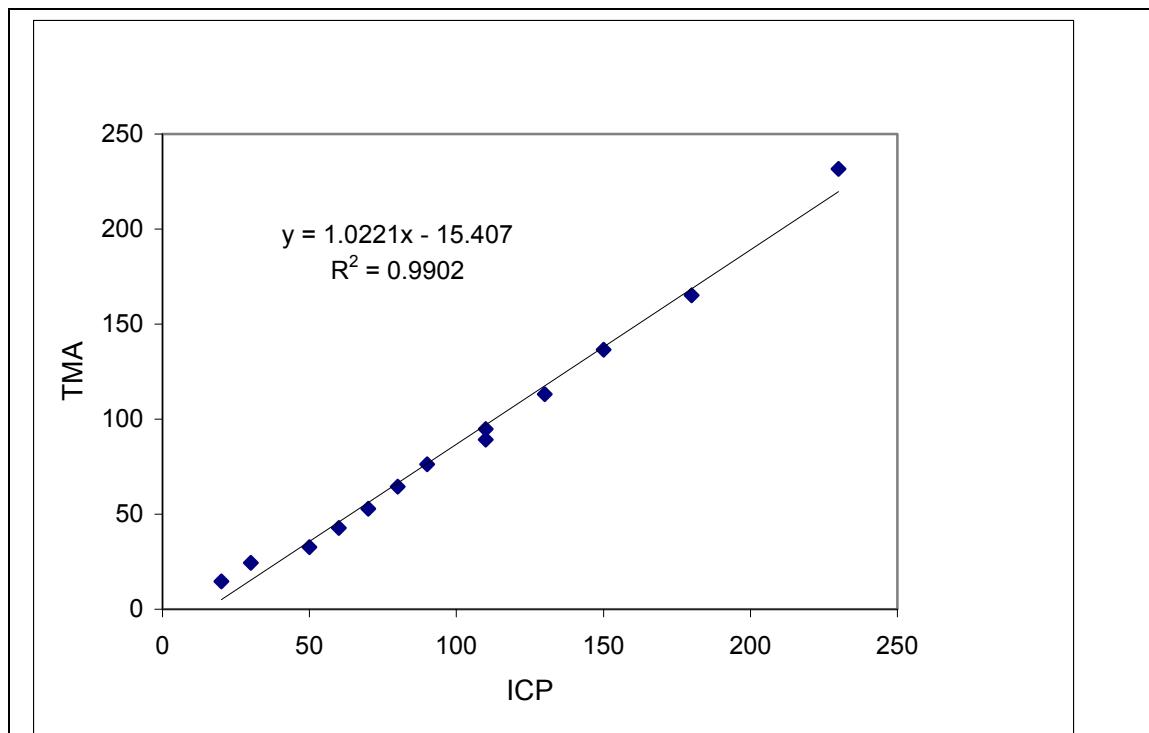
Figure 20. Comparison of the ATMA copper measurements with grab samples measured using an ICP-MS (EPA Method xxx). The ATMA measurements in µg/l are on the Y axis and the ICP-MS grab sample measurements in µg/l are on the X axis. Measurement and sampling was done at Port 6 of the MRT. Grab samples were collected every 30 minutes. The MRT was run until the copper concentration reached 230µg/l.

The second demonstration run was used to measure in real-time the actual performance of the MRT filter media. The ATMA was set to automatically measure Port 6 at 15 minute intervals and the ATMA output was calibrated to account for the 15 µg/l offset measured in the previous run. The MRT was initialized and run until the ATMA indicated break through. The results of this run can be found in Figure 21. It can be seen in this figure that breakthrough occurred after processing 1200 gallons of the waste stream.
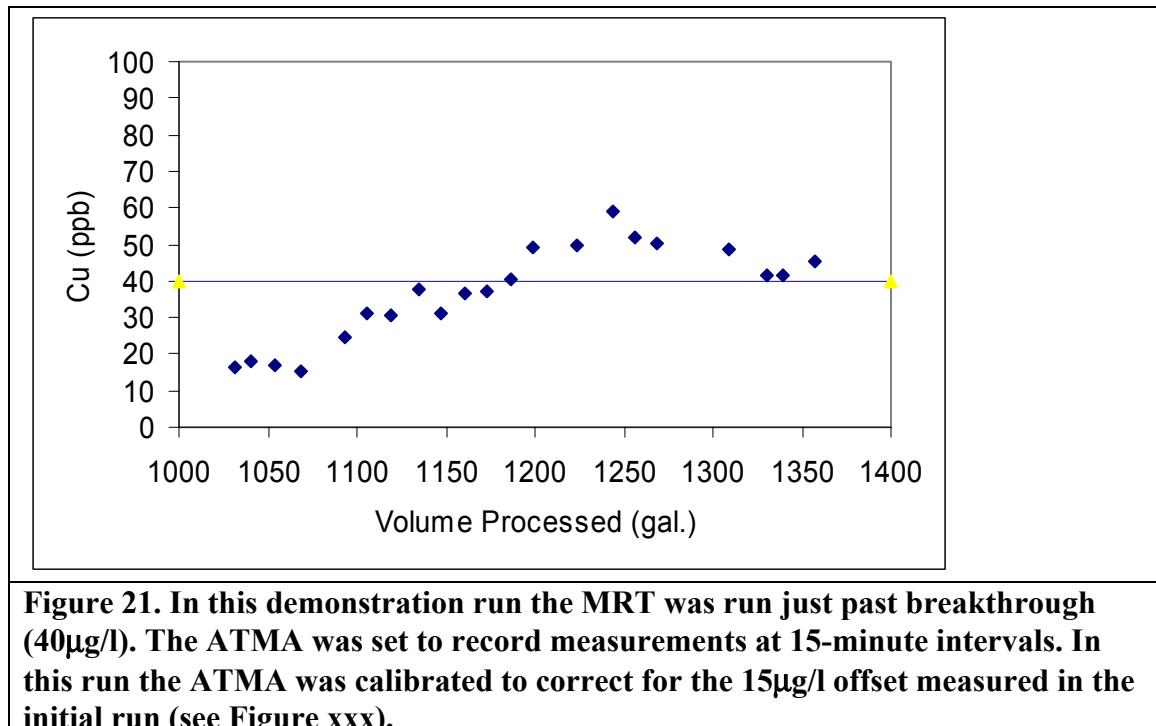
Figure 21. In this demonstration run the MRT was run just past breakthrough (40µg/l). The ATMA was set to record measurements at 15-minute intervals. In this run the ATMA was calibrated to correct for the 15µg/l offset measured in the initial run (see Figure xxx).

5.3   Technology Comparison

There is no technology comparable to the ATMA capable of measuring metal ions in solution at µg/l levels in real-time. When cost is factored in there is no comparable technology real-time or batch capable of this level of sensitivity.

The closest batch technology comparable to the ATMA is the ICP-MS and the GFAA instruments. Both these complex and large instruments are considered the standard against which all other technologies are compared. As seen in the previous section the performance of the ATMA can be equal to standard batch methods as demonstrated in the Puget Sound Naval Shipyard MRT demonstration or fall short as shown in the North Island Naval Air Station Waste Water Treatment Plant demonstration.

These two demonstrations point out the critical need to know the boundaries of the matrix test effluent before using the ATMA. Interferents, can have a dramatic affect on the accuracy of the instrument. The ATMA should be used with caution on unpredictable or unknown effluents.

6. Cost Assessment

6.1   Cost Performance

Table 11 is an estimate of the costs incurred over an expected 10 year life span of the instrument assuming a processing rate of 100 samples per month. The labor rate was fixed at $50 per hour resulting in a total life cycle cost of $207K.

Table 11. Cost performance for the Metals Analyzer over a 10 year life span.

Cost Performance					
Cost by Category					
Start-up		Operation & Maintenance		Demobilization	
Activity	$K	Activity	$K	Activity	$K
Capital Equipment	25.0	Labor	150.0	Disposal (just throw it away)	0.0
		Consumables & supplies	18.0		
		Effluent disposal	12.0		
		Training required to operate equipment	2.0		
Total	25.0	Total	182.0	Total	0.0

6.2   Cost Comparisons to Conventional and Other Technologies

Costs are best compared with current practice for determining metal ion concentrations at the IWTPs (Table 12). Typically samples are collected and preserved, the samples are then packed in ice and shipped over-night to a trace metal laboratory. Cost for the laboratory analysis can vary from $20 to $75 per sample depending on the laboratory and the volume of samples. Even at the lower $20 per sample PSA compares very favorably at less than half the cost of

conventional methods. Typically the turnaround time for conventional methods is 2-4 weeks verses 15 minutes with PSA, this allows immediate resampling if results warrant it. Using traditional methods resampling time could take over a month.

Table 12. Cost breakdown per sample between traditional laboratory GF-AA analysis and on site PSA analysis. At the two laboratories surveyed the cost of sample analysis was the same for GF-AA or ICP-MS.

Cost Breakdown Per Sample			
GF-AA		PSA	
Activity	Cost	Activity	Cost

Sample Collection ($50/hr)
 - 5 min collection
 - 10 min preservation, labeling
   packing
 - shipping
	4.17
	 8.34
	
	 1.86
		Sample Collection and Analysis
		   ($50/hr.)
		 - 5 min collection time
		 - 10 min operator time
			
			 4.17
			 8.34

Sample Analysis (contract with laboratory	50.00	Consumables - Reagents - Electrodes	 1.25 0.25
		Capital Cost of Instrument - $25k/40,000 samples	0.63
		Haz/Mat Disposal (3ml)	1.00
Total	64.37		15.64

7. Regulatory Issues

7.1   Approach to Regulatory Compliance and Acceptance

After surveying wastewater treatment plant operators it was decided that this demonstration would examine the usefulness of the ATMA for continuously monitoring the "end of process" in wastewater treatment. Currently, regulators require wastewater treatment plants to monitor their process via scheduled grab samples. These samples are measured using EPA accepted methods. The frequency of the samples is typically determined in the treatment plants National Pollutant Discharge Elimination System permit. Use of the ATMA ensures that this permitted sampling process will always meet regulatory discharge requirements. In these demonstrations the ATMA is not intended to replace EPA methods or permit required sampling, as such regulatory acceptance was not sought.

8. Technology Implementation

8.1 DoD Need

Metal contamination has been identified ant over 900 military sights. Typical military activities associated with heavy metal contamination include plating operations motor pool activities, metal finishing and cooling water treatment. These discharges are typically treated at military industrial wastewater treatment plants on base. Real-time sensors to monitor treated effluent flows will allow operators to rapidly correct for failures in the treatment process before costly exceedences occur.

8.2 Transition

The ATMA was licensed commercially to Environmental Technologies Group (ETG) Commercial Products Division and was produced in 1997 under the name Metalizer 5000. Transition of ATMA technology and ongoing developments were subject to a Cooperative Research and Development Agreement with Environmental Technologies Group. The Navy maintains a laboratory, portable and a survey ship instrument for demonstration.

Unfortunately, the Commercial Products Division of ETG was closed and production of the Metalizer 5000 was discontinued. We are currently (2002) negotiating a licensing agreement with Trace Detect Inc. for the technology. Trace Detect Inc. wants to use the technology with their existing commercial microelectrodes and miniaturized electronics. This would result in a less expensive and more compact package with no loss in features.

9. Lessons Learned

After working on two ESTCP projects the most difficult problem encountered for both was technology transfer to the commercial sector. Commercial production of this type of instrumentation is critical to its successful transition and wide spread use. Commercial partners often have conflicting goals when compared to those of the technology originator. For example in this project the initial CRADA partner began manufacturing the instrument with a list price of $30,000. The ATMA cost $10,000 in parts and labor to produce using engineers and technicians to hand build the instrument.   This high price led to the eventual demise of the product and of the commercial division manufacturing the product. After the commercial division was eliminated the parent company refused to relinquish the technology rights, making it impossible to transfer them to another company until recently. The main lesson learned is to be very careful

in selecting a commercial partner. Make sure they have the financial and technical capability to launch a new product and that they have a proven track record in the field.

10. References

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Appendix A
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Appendix B
Data Archiving

The raw and processed data for the TMA and laboratory analysis has been assembled and archived on CD-ROM and are included in this report. The raw data is in comma separated values and the laboratory data is in Microsoft Excel spread sheets.